

The University of Chicago

THE CRYSTAL STRUCTURE OF LITHIUM HYDROXIDE MONOHYDRATE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
UNIVERSITY OF CHICAGO

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By

RAYMOND PEPINSKY

Reprinted from *Zeitschrift für Kristallographie (A)*
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Crystal Structure of Lithium Hydroxide Monohydrate¹⁾.

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Introduction.

Lithium hydroxide monohydrate, $\text{LiOH} \cdot \text{H}_2\text{O}$, the "lithium hydrate" of commerce, was described crystallographically by V. von Lang²⁾ as monoclinic prismatic, with the axial ratios $a : b : c = 0.8184 : 1 : 0.3750$ and $\beta = 94^\circ 29'$.

The crystals used in the present investigation were from Merck and Company, New York. Although the faces were poorly developed, it was not necessary to recrystallize the material.

Observations.

Oscillation and complete rotation photographs about all three axes were taken, using $\text{Cu } K\alpha$ radiation and a cylindrical camera of three centimeter radius. The oscillations were of 15° range with 5° overlapping, and almost all reflections occurred on more than one film. The photographs were indexed by Bernal's graphical method³⁾, and intensities were visually estimated.

Structure factors were obtained from observed intensities with the use of the formula

$$I = K \cdot \frac{1 + \cos^2 2\theta}{\sin \Psi \cdot \cos \Phi} \cdot FF^*$$

θ = the Bragg angle,

Ψ = the azimuth of a reflection,

Φ = the elevation angle of the layer line,

and K = a constant.

Absorption was small and was neglected. Temperature and extinction effects were also neglected.

The atomic scattering factors of James and Brindley⁴⁾ were used.

1) Results of this investigation were reported at the two hundred and twenty-seventh meeting of the American Physical Society in Washington, D. C., April 27, 1939, and appeared in abstract in the report of that meeting in *Physic. Rev.* **55** (1939) 1115.

2) P. Groth, *Chemische Krystallographie*, I, (Verlag von Wilhelm Engelmann, 1906), p. 604.

3) J. D. Bernal, *Proc. Roy. Soc. London (A)* **113** (1926) 417.

4) R. W. James and G. W. Brindley, *Philos. Mag.* **12** (1932) 81.

Unit Cell and Space Group.

Oscillation photographs taken about the prism zone and indexed according to von Lang's axes indicated a body-centered cell. Transformation to a base centered cell resulted in the proper axes, with $a = 7.37 \text{ \AA}$, $b = 8.26 \text{ \AA}$, $c = 3.19 \text{ \AA}$, $\beta = 110^\circ 18'$, and $a:b:c = 0.892:1:0.386$. For a base-centered cell von Lang's ratios become $a:b:c = 0.8732:1:0.3750$, with $\beta = 112^\circ 42'$. This large discrepancy is due in part to poorly developed faces on von Lang's crystals, evidenced in the poor agreement between observed and calculated interfacial angles reported by him¹).

The measured density of 1.51 gr./cm.^3 led to $3.98 \approx 4$ molecules per cell.

No regular extinctions occur other than (hkl) absent for $h+k$ odd. This is the criterion for the space-group $C_{2h}^3-C 2/m$ or either of its subgroups C_s^3-Cm and $C_2^3-C 2$. Choice between these could be made only on the basis of the complete structure. Since the holohedral group was most probable, it was first assumed. This assumption led to the proper structure and was thereby justified.

The symmetry elements of C_{2h}^3 are two sets of two-fold axes parallel to the y -axis (i. e., parallel to b), one set passing through $(0^\circ, y, 0^\circ)$ and $(180^\circ, y, 0^\circ)$, and the other set through $(0^\circ, y, 180^\circ)$ and $(180^\circ, y, 180^\circ)$ ²). These axes are perpendicular to reflection planes $y=0^\circ$ and $y=180^\circ$. General positions are eight-fold equivalent, while points in symmetry planes or on two-fold axes are four-fold equivalent. Two-fold equivalent centers of symmetry are produced at the intersections of two-fold axes with reflection planes, and four-fold equivalent centers at the representative points $(90^\circ, 90^\circ, 0^\circ)$ and $(90^\circ, 90^\circ, 180^\circ)$.

Possible Oxygen Arrangements.

The main contribution to the scattering is from the oxygens, and their disposition was first considered.

Because of the usual oxygen bond directions, it was not considered possible for oxygens to lie in centers of symmetry. From the chemical nature of the compound it was probable that of the eight oxygens per cell four were associated with hydrogens as hydroxyl groups, and the other four were associated with pairs of hydrogens as water groups; and consequently oxygens were not in eight-fold equivalent positions.

1) In Groth, Chem. Kryst., I, loc. cit.

2) For convenience in calculating structure factors, angular parameters are used throughout this paper.

One expects to find each lithium surrounded by a tetrahedron of oxygens, the lithium-oxygen separation being about $2.0 \text{ \AA}$ and the oxygen-oxygen distance in the tetrahedron about $3.2 \text{ \AA}$. Marked deviations from these separations are unlikely, and on these grounds two further arrangements of oxygens can be excluded:

1. all oxygens in reflection planes only;
2. all oxygens on two-fold axes only.

In the first case, since the distance between reflection planes is $b/2 = 4.13 \text{ \AA}$, both bonding in the y -direction and a suitable arrangement of oxygens around a lithium is impossible.

In the second case, limitde positions of both lithiums and oxygens and the large separations between oxygens in all directions except those parallel to the plane of the b and c axes again do not permit a proper distribution of oxygens about lithiums. Oxygens are confined on the two-fold axes to regions bounded by points $1.25 \text{ \AA}$ from reflection planes (because an oxygen cannot come closer than $2.5 \text{ \AA}$ to its image on the other side of the plane). Except in the c -direction, the closest approach of two two-fold axes is $3.47 \text{ \AA}$ —which is the separation between axes ($0^\circ, y, 0^\circ$) and ($180^\circ, y, 180^\circ$). Since lithiums must lie in two-fold axes or reflection planes, and cannot lie in symmetry centers, it is entirely impossible to obtain an acceptable structure under these conditions.

The remaining possibility in this space-group is that four oxygens lie in reflection planes and four on one set of two-fold axes. In the next sections it will be shown that this is the actual arrangement.

Determination of Approximate Oxygen Parameters.

In the case to be considered, the eight oxygens lie in the following positions:

On two-fold axes	In reflection planes
$0^\circ, y_2^\circ, 0^\circ;$	$x_p^\circ, 0^\circ, z_p^\circ;$
$0^\circ, -y_2^\circ, 0^\circ;$	$-x_p^\circ, 0^\circ, -z_p^\circ;$
$180^\circ, 180^\circ + y_2^\circ, 0^\circ;$	$180^\circ + x_p^\circ, 180^\circ, z_p^\circ;$
$180^\circ, 180^\circ - y_2^\circ, 0^\circ;$	$180^\circ - x_p^\circ, 180^\circ, z_p^\circ.$

Thus three parameters are to be determined for the oxygens.

The structure factor for oxygens alone reduces to

$$F_{hkl} = 4f_{0hkl} [\cos ky_2 + \cos (hx_p + lz_p)].$$

As mentioned in the last section, an oxygen not in a reflection plane cannot lie closer than $1.25 \text{ \AA}$ to the plane. The minimum value for y_2

is thus $\frac{1.25}{8.26} \times 360^\circ = 53^\circ$. One of the oxygens on the axes always has a parameter in the first quadrant, and hence $53^\circ \leq y_2 \leq 90^\circ$.

In table I a comparison between oxygen structure factors and observed intensities of $(0k0)$ reflections is made. Without recourse to the more exact relation between intensities and structure factors, and only roughly taking into account the fall of atomic scattering power with increasing k , a value of about 75° obtained for y_2 should be very close to the actual value.

Table I. Permitted Range of y_2 , from $(0k0)$ Intensities.

$0k0$	I	$F_0/4f_0$	$\cos ky_2$	$53^\circ \leq y_2 \leq 90^\circ$
020	vw —	$1 + \cos 2y_2$	large —	$60^\circ \leq y_2 \leq 90^\circ$
040	m	$1 + \cos 4y_2$	med +	$75^\circ \leq y_2 \leq 90^\circ$
060	w —	$1 + \cos 6y_2$	0	$\approx 75^\circ$
080	vvw +	$1 + \cos 8y_2$	med —	$60^\circ \leq y_2 \leq 78^\circ$
0,10,0	vw +	$1 + \cos 10y_2$	large +	$65^\circ \leq y_2 \leq 80^\circ$

Using the value of 75° for y_2 , a similar comparison between intensities and the oxygen structure factors for $(h00)$ and $(hk0)$ reflections leads to an approximate value of 103° for x_p . Finally, a study of $(00l)$ and $(0kl)$ reflections results in values of $\pm 143^\circ$ for z_p . An examination of $(h0l)$ reflections leads to the discarding of the negative value.

Table II shows a sample check for general reflections, involving a comparison of observed and calculated factors for oxygens alone. Later addition of lithium contributions improves the agreement.

Table II. Comparison between Observed and Calculated Structure Factors for $(2k1)$ and $(2k\bar{1})$ Reflections.

$2k1$	I	$(F/4)_0$ calc.	$(F/4)_0$ obs.
201	ms	$4.5(1 + .95) = 8.9$	6.7
221	vvw —	$4.0(-.87 + .98) = 0.5$	1.4
241	mw	$3.3(.50 + .98) = 4.9$	4.6
261	vvw —	$2.6(0 + .98) = 2.6$	2.1
281	f. trace	$2.0(-.50 + .98) = 1.0$	0.8
$2k\bar{1}$	I	$(F/4)_0$ calc.	$(F/4)_0$ obs.
20 $\bar{1}$	s	$5.5(1 + .45) = 8.0$	5.9
22 $\bar{1}$	vw +	$5.1(-.87 + .45) = -2.2$	1.6
24 $\bar{1}$	w +	$3.9(.50 + .45) = 3.7$	3.6
26 $\bar{1}$	t —	$2.9(0 + .45) = 1.3$	1.4
28 $\bar{1}$	abs.	$2.1(-.50 + .45) = -0.1$	0
2,10, $\bar{1}$	w	$1.7(.87 + .45) = 2.3$	3.0

Similar agreement for a large number of reflections establishes the essential correctness of the oxygen distribution, while simultaneously confirming the space-group C_{2h}^3 .

Two-Dimensional Fourier Analyses and Determination of Lithium Positions.

For $(h0l)$ reflections the structure factor for oxygens alone is

$$F_{0h0l} = 4f_{0h0l} [1 + \cos(hx_p + lz_p)],$$

which can never have a negative value. Whenever a complete structure factor becomes negative as a result of the lithium contribution, it will be quite small. Consequently the signs of all important structure factors are known to be positive, and parameters for the oxygens in the reflection

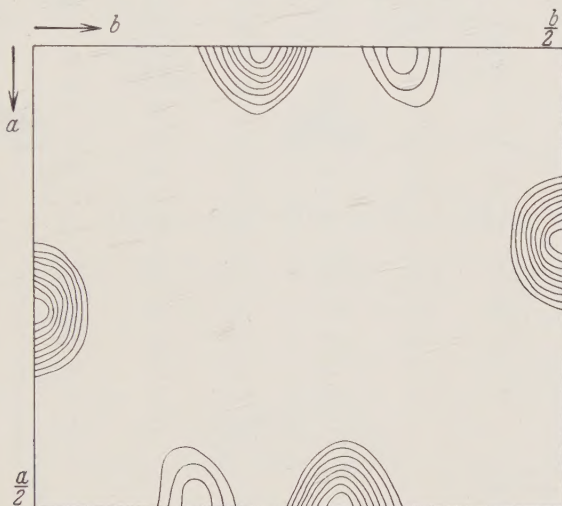


Fig. 1. Fourier-Projection on (001). Only one fourth of the cell is shown.

planes can be found directly from a Fourier projection on (010). Such an analysis does of course depend upon knowledge of the space group and the presence of some oxygens in the reflection planes—all of which was established simultaneously with the approximate parameters in the last section.

Using the approximate parameters already obtained, the signs of the factors for $(hk0)$ and $(0kl)$ reflections could also be calculated, small factors with consequent doubtful signs being omitted. A Fourier projection on (001) was first made, and is shown after later improvement in figure 1. (Only the first quarter of the cell is shown). The oxygens

on the two-fold axes and in the reflection planes both appear, and in addition a fine lithium maximum occurs at $x = 0^\circ$, $y \approx 125^\circ$. After calculating the signs of terms previously neglected and adding them to the projection, the parameters

$$y_2 = 76^\circ, \quad x_p = 103^\circ, \quad y_{Li} = 126^\circ$$

were obtained.

The lithiums cannot lie on the same two-fold axes as the oxygens, if the lithium-oxygen distance is not to be too small. Hence they must



Fig. 2. Fourier-Projection on (010).

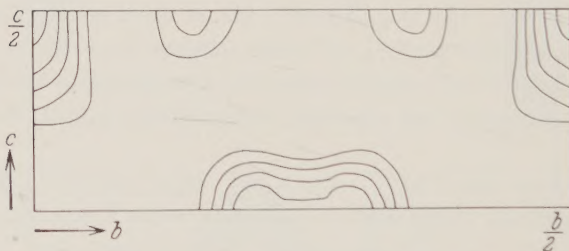


Fig. 3. Fourier-Projection on (100).

Only one fourth of the cell is shown,

lie on the other set of axes, at $z = 180^\circ$. This is confirmed in the projections on the (010) and (100) planes, shown in figures 2 and 3 respectively.

These three projections result in the complete set of positions:

O_2	O_p	Li
$0^\circ, 76^\circ, 0^\circ;$	$103^\circ, 0^\circ, 140^\circ;$	$0^\circ, 126^\circ, 180^\circ;$
$0^\circ, 284^\circ, 0^\circ;$	$257^\circ, 0^\circ, 220^\circ;$	$0^\circ, 234^\circ, 180^\circ;$
$180^\circ, 256^\circ, 0^\circ;$	$283^\circ, 180^\circ, 140^\circ;$	$180^\circ, 306^\circ, 180^\circ;$
$180^\circ, 104^\circ, 0^\circ.$	$77^\circ, 180^\circ, 220^\circ.$	$180^\circ, 54^\circ, 180^\circ.$

The relations between observed and calculated structure factors are shown in tables III, IV, V and VI.

Table III.
Observed and Calculated Structure Factors: ($h k 0$)
Reflections.

$h k 0$	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$	$h k 0$	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$
200	.14	42	27	26	330	.29	7	16	12
400	.29	120	67	80	350	.37	35	43	49
600	.43	13	29	33	370	.47	9	23	-19
800	.58	13	21	22	390	.58	25	31	32
020	.12	16	11	2	420	.31	7	11	-15
040	.24	90	51	60	440	.38	11	22	25
060	.36	30	39	40	460	.46	9	23	21
080	.49	12	28	18	480	.57	0	0	7
0100	.61	20	26	24	510	.36	18	31	-29
110	.10	9	10	-12	530	.40	19	34	-34
130	.23	65	38	-28	550	.47	0	0	1
150	.36	27	33	23	570	.56	38	42	-45
170	.51	29	42	37	620	.45	16	32	-30
190	.55	7	18	17	640	.50	0	0	0
220	.19	250	73	102	660	.57	0	0	0
240	.28	35	36	-27	710	.51	10	24	21
260	.39	8	21	-19	730	.54	8	19	17
280	.51	18	33	-25	820	.59	17	22	-22
2100	.62	2	7	-9	840	.63	0	0	0
310	.23	31	29	33					

Table IV.
Observed and Calculated Structure Factors: ($0 k l$)
Reflections (Excepting ($0 k 0$) Reflections.)

$0 k l$	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$	$0 k l$	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$
001	.19	0	0	-6	022	.36	37	24	-26
002	.33	55	50	55	042	.42	2	11	10
003	.50	10	18	23	062	.49	5	17	9
021	.21	160	62	80	082	.59	0	0	-1
041	.29	4	10	4	023	.51	2	10	-5
061	.40	24	38	36	043	.56	18	26	27
081	.51	12	26	-28	063	.62	0	0	1
0101	.63	5	11	7					

Table V. Observed and Calculated Structure Factors: ($h0l$) Reflections Excepting ($h00$) and ($00l$).

hkl	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$	$h0l$	$\sin \theta/\lambda$	$I_{\text{obs.}}$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$
201	.25	90	67	72	20 $\bar{2}$	.32	60	63	61
401	.38	6	22	-12	40 $\bar{2}$	.36	11	32	22
601	.51	13	33	29	60 $\bar{2}$	.45	20	45	59
20 $\bar{1}$	.18	120	59	59	80 $\bar{2}$	.56	0	0	9
40 $\bar{1}$	.28	11	25	26	203	.57	7	22	26
60 $\bar{1}$	.41	0	0	3	20 $\bar{3}$	.47	0	0	-7
80 $\bar{1}$	.55	12	32	27	40 $\bar{3}$	.49	13	35	36
202	.41	8	28	23	60 $\bar{3}$	.54	2	12	-8
402	.51	15	36	51	80 $\bar{3}$	.62	15	20	-4

Table VI. Observed and Calculated Structure Factors: General Reflections.

hkl	$\sin \theta/\lambda$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$	hkl	$\sin \theta/\lambda$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$
111	.21	8	0	261	.44	21	13
131	.27	47	-62	281	.55	8	-9
151	.36	24	16	22 $\bar{1}$	.21	16	-18
171	.47	26	-25	24 $\bar{1}$	.30	36	50
191	.58	0	2	26 $\bar{1}$	.40	14	-15
11 $\bar{1}$	.17	52	71	28 $\bar{1}$	.52	0	-2
13 $\bar{1}$	.24	26	-10	210 $\bar{1}$	.63	30	27
15 $\bar{1}$	.34	52	59	222	.42	36	-44
17 $\bar{1}$	.45	11	15	242	.47	15	-10
19 $\bar{1}$	.57	22	26	262	.55	6	-7
112	.37	30	28	282	.63	23	-14
132	.41	22	18	22 $\bar{2}$	.34	24	-24
152	.47	37	45	24 $\bar{2}$	.40	13	14
172	.56	16	-10	26 $\bar{2}$	.48	20	12
11 $\bar{2}$	.32	36	-35	28 $\bar{2}$	.58	6	0
13 $\bar{2}$	.36	36	-40	223	.58	16	-16
15 $\bar{2}$	.44	0	-2	243	.62	14	16
17 $\bar{2}$	.53	46	-51	22 $\bar{3}$	.49	33	-36
19 $\bar{2}$	.63	8	1	24 $\bar{3}$	.53	0	2
113	.57	8	-9	26 $\bar{3}$	.60	21	-24
133	.56	34	-40	311	.32	18	17
153	.61	0	-4	331	.36	34	-34
11 $\bar{3}$	.49	27	28	351	.44	26	25
13 $\bar{3}$	.51	14	9	371	.53	18	-11
153	.57	32	32	31 $\bar{1}$	.23	26	-26
221	.29	14	9	33 $\bar{1}$	.29	53	80
241	.35	46	62	35 $\bar{1}$	.38	0	-1

Table VI (continued).

hkl	$\sin \theta/\lambda$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$	hkl	$\sin \theta/\lambda$	$\pm k$ $\cdot F_{\text{obs.}}$	2.5 $\cdot F_{\text{calc.}}$
37 $\bar{1}$	.48	32	35	53 $\bar{1}$	.39	0	- 3
39 $\bar{1}$	.59	11	- 8	55 $\bar{1}$	.45	32	48
312	.46	19	-17	57 $\bar{1}$	.55	11	9
332	.49	21	-21	512	.57	0	4
352	.55	14	6	532	.60	0	1
31 $\bar{2}$	.34	29	30	51 $\bar{2}$	.40	17	-18
33 $\bar{2}$	.38	18	18	53 $\bar{2}$	.44	22	-21
35 $\bar{2}$	.48	32	45	55 $\bar{2}$	.50	0	8
37 $\bar{2}$	.54	10	-11	51 $\bar{3}$	.51	8	9
313	.62	18	26	533	.54	23	24
31 $\bar{3}$	.47	0	4	621	.53	0	1
33 $\bar{3}$	.51	27	-33	641	.57	33	32
35 $\bar{3}$	.56	16	11	62 $\bar{1}$	.43	32	32
421	.40	41	-50	64 $\bar{1}$	.47	13	11
441	.45	0	- 1	661	.55	21	-18
461	.53	29	-30	62 $\bar{2}$	.46	0	- 2
481	.60	30	-27	64 $\bar{2}$	.51	20	25
42 $\bar{1}$	.30	31	-27	62 $\bar{3}$	.55	33	-34
44 $\bar{1}$	.37	28	30	711	.59	6	- 5
46 $\bar{1}$	.46	13	-11	731	.61	32	-32
48 $\bar{1}$	.58	11	- 9	71 $\bar{1}$	.54	10	- 5
422	.53	0	- 3	73 $\bar{1}$	.57	31	-35
442	.57	18	21	75 $\bar{1}$	.62	0	3
42 $\bar{2}$	.38	38	-53	71 $\bar{2}$	.51	0	3
44 $\bar{2}$	.44	14	-14	73 $\bar{2}$	.53	0	- 2
46 $\bar{2}$	.51	0	-10	713	.58	18	19
42 $\bar{3}$	.50	0	5	73 $\bar{3}$	.60	11	-11
44 $\bar{3}$	.54	28	38	82 $\bar{1}$	.56	0	2
511	.46	26	23	84 $\bar{1}$	.60	29	31
531	.48	18	-18	82 $\bar{2}$	.57	32	-38
551	.54	29	27	91 $\bar{1}$	.62	18	18
51 $\bar{1}$	.35	38	48	91 $\bar{2}$	.62	6	5

Discussion of the Structure.

Each lithium is properly at the center of a tetrahedron of oxygens. Two such tetrahedra share an edge in a reflection plane. Upper and lower corners are shared with tetrahedra in cells above and below, resulting in unending chains of paired tetrahedra in the direction of the c -axis. These chains are linked sideways by hydroxyl bonding.

In figure 4 the structure is shown projected on the (010) plane. Small doubled circles represent lithiums, two being superposed in the projection due to the reflection plane. Similarly, large doubled circles

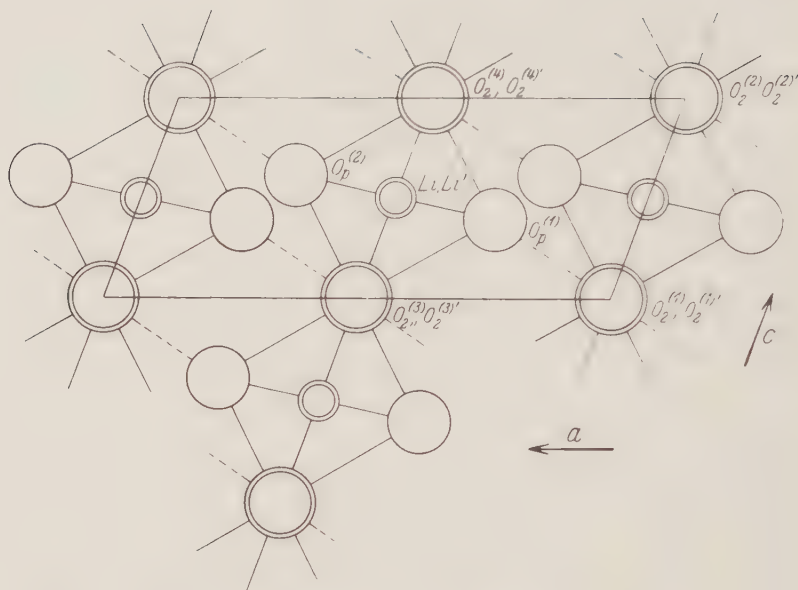


Fig. 4. Projection of Structure on (010).

indicate the two superposed oxygens on the two-fold axes. Single large circles represent oxygens in the reflection planes.

Ionic separations are indicated in table VII, the ions being labelled as in figure 4. Underlined entries correspond to distances within a single tetrahedron.

Table VII. Ionic Separations in $\text{LiOH} \cdot \text{H}_2\text{O}$.

	$O_p^{(2)}$	$O_2^{(3)}$	$O_2^{(4)}$	$\text{Li}^{(1)}$	$O_2^{(1)}$	$O_2^{(2)}$	$O_2^{(1)'} $
$O_p^{(1)}$	<u>2.99</u>	3.34	3.14	1.95	2.68	3.76	2.68
$O_p^{(2)}$		3.14	3.34	1.95			
$O_2^{(3)}$			3.19	1.97	3.74		3.74
$O_2^{(4)}$				1.97		3.74	
$O_2^{(1)}$						3.19	3.48
$\text{Li}^{(2)}$				2.48			

Hydrogen Positions and Nature of Bonding.

The distance of 2.68 Å between corners of adjacent tetrahedra indicates hydroxyl bonding¹⁾ of these oxygens. Two such hydroxyl bonds reach from each oxygen on a two-fold axis to two oxygens in the nearest

1) The term "hydroxyl bonding" is used in the sense discussed by J. D. Bernal and H. D. Megaw, Proc. Roy. Soc. London (A) **151** (1935) 384.

reflection plane, and each oxygen in a plane is bonded similarly to two oxygens on axes. The angle between the bonds from an axis oxygen is 100° , and from a plane oxygen is 80° .

In this way eight hydrogens of the twelve per cell are accounted for as lying in general, eight-fold-equivalent positions. But whether these eight are associated most closely with axis oxygens or with plane oxygens remains to be determined. The key to a decision lies in consideration of the disposition of the remaining four hydrogens per cell. Two possibilities need to be examined:

1. The four non-general hydrogens are associated closely with axis oxygens, and the eight hydrogens of the hydroxyl bonds with plane oxygens. The axis oxygens are then in hydroxyl groups, and the plane oxygens in water groups.

2. The four hydrogens are associated closely with plane oxygens into hydroxyl groups, while the eight hydrogens of the hydroxyl bonds form water groups with the axis oxygens.

In the first case, because of the positions of the lithiums the four hydrogens would have to lie on the same axes as the oxygens and between the oxygens and their nearest reflection planes. The bond from an axis oxygen to its associated hydrogen would then bisect the angle of 100° between the hydroxyl bonds which reach that oxygen, resulting in highly improbable angles between all three bonds. The distance between axis oxygens across the nearest reflection plane is $3.48 \text{ \AA}$; and in the event that these oxygens were in hydroxyl groups, the hydroxyls would be very weakly bonded across the plane if at all. On the other hand, oxygens in the plane have a closest distance of approach of $2.99 \text{ \AA}$, when they form the common edge of mirrored tetrahedra. This is the smallest separation between any pair of oxygens in the tetrahedra, and can be accounted for somewhat as the result of the proximity of two lithiums; even so it seems unlikely that oxygens in water groups would have this smallest separation.

The second case avoids all these difficulties, and is as probable as the first case is improbable. Here water groups exist on the axis, with an angle of 100° between the bonds. The distance of $3.48 \text{ \AA}$ between water oxygens not coordinated to the same lithium is quite acceptable. Hydroxyl groups now lie in the plane, and have a separation of $2.99 \text{ \AA}$ between their oxygens—which is logically the smallest oxygen-oxygen separation in a tetrahedron. The angle between the bond from the plane oxygen to its hydrogen and the hydroxyl bond reaching the plane oxygen can be 100° or more.

The conclusions are then that the oxygens on the axes are in water groups, and the oxygens in the planes are in hydroxyl groups. Hydroxyl bonding occurs between waters and hydroxyls.

The lithium oxygen separation is 1.95 Å and 1.97 Å. In the tetrahedra the $O_{H_2O} - O_{H_2O}$ separation is 3.49 Å; the $O_{OH} - O_{OH}$ separation is 2.99 Å; while the $O_{H_2O} - O_{OH}$ separations of 3.44 and 3.34 Å occur. The types of bonding and bond directions and electrostatic conditions contribute in involved ways to the distortion of the tetrahedra.

Comparison with Li_2O and $LiOH$ Structures.

Li_2O has a fluorite-type structure¹⁾, with lithiums in the fluorine positions and oxygens in place of the calciums. Lithiums lie at the center of perfect oxygen tetrahedra, and atomic separations are:

$$Li-O = 2.00 \text{ Å}, \quad Li-Li = 2.32 \text{ Å}, \quad O-O = 3.27 \text{ Å}.$$

These are similar to the separations observed in $LiOH \cdot H_2O$, except that the $Li-Li$ separation in the latter crystal is larger—due perhaps to the strong binding and consequent reduction in separation between the hydroxyl groups in the reflection planes.

For $LiOH$ Ernst¹⁾ reports a structure based upon layers of hydroxyl tetrahedra. Alternate layers have their tetrahedra completely filled with lithiums, but tetrahedra between these are completely empty. For the filled tetrahedra the reported separations are:

$$Li-OH = 1.97 \text{ Å},$$

$$Li-Li = 2.51 \text{ Å},$$

$$OH-OH = 3.05 \text{ Å}, \text{ for two edges of a tetrahedron.}$$

$$OH-OH = 3.55 \text{ Å}, \text{ for remaining two edges of the tetrahedron.}$$

Thus the tetrahedra are very much distorted. The first three separations agree well with those in the $LiOH \cdot H_2O$ tetrahedra, but the fourth does not.

The unfilled tetrahedra have two edges of 3.55 Å and two of 3.61 Å. Bonding between layers is thus very weak. The complete cleavage parallel to the layers is in agreement with this feature of the structure.

Summary.

$LiOH \cdot H_2O$ is monoclinic prismatic, with axes $a = 7.37 \text{ Å}$, $b = 8.26 \text{ Å}$, $c = 3.49 \text{ Å}$, $\beta = 110^\circ 18'$, and the axial ratios $a:b:c = 0.892:1:0.386$. The density is 1.51 gr. cc., and there are four molecules per cell. The

1) E. Zintl, A. Harder, B. Dauth, Z. Elektrochem. **40** (1934) 588.

2) Th. Ernst, Z. physik. Chem. (B) **20** (1933) 65.

space group is $C_{2h}^3-C 2/m$, which has reflection planes at $y = 0^\circ$ and $y = 180^\circ$, and two sets of two-fold axes perpendicular to these planes. Each lithium is at the center of a tetrahedron of oxygens. Two such tetrahedra share an edge in a reflection plane and at an angle of 12.5° with the a -axis. Upper and lower corners of all tetrahedra are shared with tetrahedra in the cells immediately above and below, the edges between these shared corners being parallel to the c -axis. Thus paired tetrahedra form unending chains in the c -direction.

Oxygens of the shared tetrahedron edges in reflection planes are in hydroxyl groups, and oxygens of upper and lower tetrahedron corners are in water groups. The chains of paired tetrahedra are linked sideways by hydroxyl bonding between the hydroxyls and waters.

Separations between atoms within a tetrahedron are:

$$\begin{array}{ll} Li-O_{OH} = 1.95 \text{ \AA}, & O_{OH}-O_{H_2O}^{(1)} = 3.14 \text{ \AA}, \\ Li-O_{H_2O} = 1.97 \text{ \AA}, & O_{H_2O}^{(1)}-O_{H_2O}^{(2)} = 3.19 \text{ \AA}, \\ O_{OH}-O_{OH} = 2.99 \text{ \AA}, & O_{OH}-O_{H_2O}^{(2)} = 3.34 \text{ \AA}. \end{array}$$

Separations for nearest atoms in adjacent tetrahedra are:

$$\begin{array}{ll} Li-Li = 2.48 \text{ \AA}, & O_{H_2O}^{(1)}-O_{H_2O}^{(1)} = 3.48 \text{ \AA}, \\ O_{OH}-O_{H_2O} = 2.68 \text{ \AA}, & O_{OH}^{(1)}-O_{OH}^{(3)} = 3.74 \text{ \AA}. \end{array}$$

Relations between this structure and those given elsewhere for Li_2O and $LiOH$ are discussed.

Acknowledgement.

The author has had the honor and privilege of working under Professor W. H. Zachariasen, and wishes to express deepest gratitude to Professor Zachariasen for his constant aid and advice in this and all other problems in which the writer has been engaged while at Ryerson Physical Laboratory.

Received August 3, 1939.

